APPENDIX E

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Contributions to Light Extinction During Project MOHAVE

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ABSTRACT

The contribution of aerosols to light extinction at Meadview, AZ during summer, 1992 was estimated using Mie theory and size-resolved aerosol chemical measurements. Sulfate particle size increased as a function of relative humidity. Twelve-hour average light scattering was estimated to within 15%. Sulfate was the most abundant chemical component in the fine aerosol fraction. On average, Rayleigh scattering, coarse particles, and fine sulfates contributed 39, 21, and 19% to total light extinction. Average estimated light scattering was largely insensitive to assumptions about mixing state, degree of sulfate neutralization and organic carbon water uptake properties. It was estimated that a reduction of Mohave Power Plant (MPP) SO_2 emissions corresponding to a contribution of 19% to ambient sulfate would have resulted in a decrease in total light extinction of between 3.3 and 5.3%.

INTRODUCTION

The objective of Project MOHAVE (Measurement of Haze and Visual Effects) was to determine the effect of emissions from the Mohave Power Plant (MPP) and other significant sources in the southwestern U.S. on visibility in the Grand Canyon National Park. MPP's impact on visibility would result from primary particle emissions and from sulfate particles formed by the oxidation of MPP sulfur dioxide. To determine this effect, it is necessary to estimate the contribution of MPP to ambient sulfate and this is the goal of several independent modeling studies associated with Project MOHAVE. The objective of this study is to estimate particle light extinction based on physico-chemical measurements at Meadview, AZ, located on the northwestern rim of the Grand Canyon, during summer, 1992, and to simulate the effects of reducing MPP sulfur emissions on light extinction.

The light extinction coefficient for particles (Bep) is the sum of the particle scattering (Bsp) and absorption (Bap) coefficients. It is equal to the number of particles (n) multiplied by their extinction cross sections σ:

$$\text{Bep} = \int \sigma(D)n(D)dD \qquad (1)$$

The extinction cross section (σ) depends on the wavelength of the incident light, the complex index of refraction and the diameter (D) of the particles. For spherical particles, σ may be calculated using Mie theory (Mie, 1908; Bohren and Huffman, 1983). The absorption cross section is the difference between the extinction and scattering cross sections.

In this paper, particle light extinction is estimated using Mie theory in conjunction with aerosol measurements at Meadview, AZ during summer, 1992. The effects of various assumptions about aerosol mixing state, degree of sulfate neutralization, and organic carbon chemical and water uptake properties on estimated light extinction are examined. Finally, the effects of sulfur emissions reductions on light extinction are evaluated with respect to assumptions about aerosol growth mechanisms.

METHODS

Aerosol Particle Samples

Aerosol sampling at Meadview during summer, 1992 was described by Pitchford and Green (1997) and Turpin et al. (1997). $PM_{2.5}$ (particles with diameters less than 2.5 µm) samples were acquired with IMPROVE, two-stage samplers (Malm et al., 1994). Twelve-hour duration (0700-1900 and 1900-0700 MST) samples were analyzed for PM_{10} and $PM_{2.5}$ mass, and $PM_{2.5}$ sulfate, nitrate, elements, and organic and elemental carbon (OC and EC). The $PM_{2.5}$ particle absorption coefficient (Bap) was measured by light transmission through a Teflon filter sample using the University of California at Davis (UCD) laser integrating plate method (LIPM). IMPROVE organic carbon concentrations were corrected for volatile organic compound absorption by the quartz filter by subtraction of a backup filter average (Turpin et al., 1994; 1997).

MOUDI (Micro Orifice Uniform Deposit Impactor) cascade impactor samples were collected by the University of Minnesota Particle Technology Laboratory from 0700 to 1900 MST. The MOUDI samples provided size distributions for sulfate, nitrate, ammonium, OC and EC, and element concentrations for particles with diameters less than 1.8 µm. There were 44, twelve-hour day time periods with valid concurrent IMPROVE and MOUDI concentrations.

Harvard-EPA Annular Denuder System (HEADS) samples were collected twice daily from 0700 to 1300 and from 1300 to 1900 MST to measure $PM_{2.5}$ sulfate, nitrate, ammonium, and hydrogen ion, and gaseous sulfur dioxide, nitric acid, and ammonia. Pitchford and Green (1997) and Turpin et al.

(1997) presented detailed comparisons of concentrations measured by the IMPROVE, MOUDI and HEADS samplers.

Light Extinction Modeling

Size Distributions

Winklmayr et al.'s (1990) adaptation of Twomey's (1975) nonlinear iterative algorithm was used to calculate MOUDI size distributions from the impactor stage concentrations. The result was a series of discrete values of dC/dlogD versus D (where C is concentration and D is diameter). The MOUDI inversions were based on calibration data determined for ambient conditions at Meadview (Peter McMurry, personal communication).

The MOUDI samplers contained "after filters", which collected particles that did not impact on the stages. The after filter concentrations result in part from particle bounce from the upper stages of the impactor. The size distribution of particles which may have bounced is not known. Stein et al. (1994) found that significant bounce occurred for 0.125 μm diameter particles at relative humidity less than 60-70%. On average, 17, 18, 49, 12, and 22% of total (including the after filter) sulfate, ammonium, OC, EC, and dust were found on the after filter. The large amount of OC on the quartz after filter has been attributed to absorption of gaseous organic compounds (Turpin et al., 1997). The after filter concentrations were not used to derive the MOUDI size distributions.

Chemical Concentrations

Particle light extinction was estimated by applying the abundances (expressed as a fraction of the sum of the stage concentrations excluding the after filter) of sulfate, OC, EC, and dust on the MOUDI stages to the corresponding IMPROVE filter concentrations. Nitrate was not detected in the MOUDI samples and was assumed to follow the size distributions of MOUDI sulfate. The dust component was calculated by converting the concentrations of the major crustal elements to their oxides (Zhang et al., 1994). The average of 44, day time IMPROVE sample concentrations of $PM_{2.5}$ sulfate ion, nitrate ion, OC, EC, and dust were 1.60, 0.21, 0.60, 0.15, and 0.46 μg m^{-3}, respectively. Twelve-hour average relative humidity (RH) ranged from 7 to 54% (average = 24%).

Ion and carbon concentrations were converted to their equivalent compound concentrations. The degree of sulfate neutralization was inferred from the relative abundances of ammonium and sulfate. The amount of water associated with sulfate as a function of RH depends on its chemical form, for example, sulfuric acid, ammonium bisulfate, or ammonium sulfate. Ammonium was measured in the MOUDI and HEADS but not the IMPROVE samples.

McMurry et al. (1996) and Malm et al. (1996) assumed that sulfate at Meadview during summer, 1992, was fully neutralized, as ammonium sulfate. The average molar ratio of total (including the after filter) MOUDI ammonium to sulfate was 1.77±0.27, indicating that MOUDI sulfate was fully neutralized in most cases. Based on the relative abundances of ammonium and sulfate in the MOUDI samples, sulfate would have been present as ammonium sulfate and ammonium bisulfate in 38 and 6 samples, respectively. Malm (1998) assumed that sulfate at Meadview, summer 1992, was more acidic, based on the relative abundances of sulfate, nitrate, and ammonium in the HEADS samples. For the 44 periods concurrent with the IMPROVE samples, the average molar ratio of HEADS ammonium to sulfate was 1.26±0.54. We feel that the HEADS data are suspect for several reasons. As Turpin et al. (1997) demonstrated, the HEADS ion balance shows a systematic cation deficit. For periods corresponding to the IMPROVE-MOUDI sample set, the average ratio of cations ($H^+ + NH_4^+$) to anions ($SO_4^= + NO_3^-$) was 0.82±0.26 with a range of 0.21 to 1.52. Turpin et al. (1996) concluded that even if all of the cation deficit represented error in the ammonium measurement, the aerosol would still be acidic. This explanation begs the question of the accuracy of the H^+ data. Indeed, there should be a negative correlation between H^+ and non-ammonium nitrate NH_4^+ if the major cations and anions have been accounted for. The actual correlation between 12-hour average H^+ and NH_4^+ was 0.29. Because sulfate neutralization is a potentially important issue for estimating light extinction, the sensitivity of light extinction estimates to assumptions about sulfate neutralization based on the MOUDI and HEADS data sets is examined.

Light Extinction Model

The ELSIE (Elastic Scattering Interactive Efficiencies) model was described in detail by Sloane (1986) and Lowenthal et al. (1995). It was assumed that ammonium sulfate, ammonium bisulfate, sulfuric acid, ammonium nitrate, OC, and EC were internally and homogeneously mixed but that dust was externally mixed. Particle light extinction was also estimated assuming that all components were externally mixed. The physical and optical properties of the individual chemical components are summarized in Table 1 (Sloane, 1986; Lowenthal et al., 1995). A factor is needed to convert OC carbon to compound mass, which may include hydrogen, oxygen, and other elements. However, the OC mass conversion factor, density, and refractive index were not measured during the study and may vary considerably. Tests were done to evaluate the sensitivity of estimated light extinction to assumptions about these parameters.

Water concentrations associated with ammonium nitrate, sulfuric acid, ammonium bisulfate, and ammonium sulfate were estimated as a function of RH using growth curves developed experimentally by Chan et al. (1992) and Tang and Munkelwitz (1994) for single-salt solutions. We assumed that water associated with these compounds exhibited hysteresis below the deliquescence RHs. Similarly, the hygroscopic properties of OC were assumed to be the same as those of ethylene glycol (Curme and Johnson, 1952). Because ethylene glycol is a highly water-absorbing organic compound, extinction was also estimated assuming that OC was completely insoluble. It was assumed that the water-growth properties of these components were independent, i.e., that the components did not interact in solution, and that the total aerosol liquid water was the sum of the water associated with the individual components. Elemental carbon and dust were assumed to be insoluble.

The MOUDI sampler separated particles according to their ambient or "wet" particle aerodynamic diameters. The total particle volume was calculated from the dry IMPROVE sampler masses, the densities of the individual components, and the estimated water volume. The particle density, calculated from the wet volume and wet mass, was used to convert the MOUDI aerodynamic sizes to Stokes (geometric) diameters. The number of particles was calculated from the particle volume and particle size in 16 discrete bins from 0.05 to 2.5 μm. The particle refractive index was calculated as the volume-weighted average of the refractive indices of the individual components, including water.

Light scattering and absorption were calculated at a wavelength of 0.53 μm for each size bin and summed to provide the corresponding scattering (Bsp) and absorption (Bap) coefficients. These estimates were compared to 12-hour average particle light scattering measured with an MRI Model 1560 nephelometer preceded by a 2.5 μm Bendix cyclone separator (operated by Aerosol Dynamics, Inc.) and with particle light absorption measured by the LIPM.

RESULTS AND DISCUSSION

<u>Sulfate Size Distributions</u>

Sulfate geometric mean diameters (GMDs) and standard deviations (GSTDs) were calculated for each MOUDI sample. Sulfate GMDs ranged from 0.21 to 0.38 μm and GSTDs ranged from 1.61 to

2.23. For comparison, Pitchford and Green (1997) analyzed DRUM (Davis Rotating-drum Universal-size -cut Monitoring) sulfur data from Meadview, summer, 1992, and reported GMDs ranging from 0.21 to 0.33 μm. There was a significant (α=0.05) correlation between RH and sulfate GMD (0.58), suggesting hygroscopic growth as a function of RH..

In-cloud oxidation of sulfur dioxide (SO_2) followed by aggregation and evaporation of cloud droplets is also expected to produce larger aerosol particles (Hoppel et al., 1986; Hoppel, 1988). Ames and Malm (1998) developed a "cloud interaction potential" (CIP) based on over 2000 photographs of cloud cover during the experiment. The CIP was intended as an estimate of the potential for the MPP plume to undergo in-cloud chemical processing. On a scale of 0 to 100, hourly CIP values ranged from 0 (clear sky) to 67. While there was a significant correlation (0.64) between RH and CIP, the correlation between sulfate GMD and CIP (0.25) was not significant.

Estimated Light Extinction

Light extinction was calculated under a variety of assumptions about mixing state (internal versus external mixture), sulfate neutralization, and OC mass conversion factor, density, refractive index, and water uptake. Estimated and measured scattering (Bsp) are compared in Table 2. One outlier (8/2/92) with estimated and measured Bsp of 18.3 and 6.6 Mm^{-1}, respectively, was excluded from the comparison. Because chemical concentrations, size distributions and RH (21%) for this sample were typical of those of other samples, we believe that the measured Bsp during this sample was in error.

The average measured Bsp was 10.2 Mm^{-1}. The average absolute error (AAE), the average of the absolute differences between measured and estimated Bsp divided by measured Bsp, expressed as a percent, ranged from 13.8% for an external mixture assuming zero OC water uptake (Case 4) to 22.7% for an internal mixture with an OC mass conversion factor of 1.9 (Case 9). Comparisons were somewhat better for external versus internal mixtures (Case 2 versus Case 1 and Case 4 versus Case 3). It made little difference whether the degree of sulfate neutralization was inferred from the MOUDI or HEADS data (Cases 1 and 5, respectively).

There is considerable uncertainty regarding the physical and optical properties of organic carbon (OC) in atmospheric particles. Only a small fraction, less than <20%, of the OC in remote areas like the Grand Canyon has been identified. Even a smaller fraction of water-soluble organics has been identified (Saxena and Hildemann, 1996). If OC is a major aerosol component, assumptions about its density, mass conversion factor, and hygroscopic properties will significantly affect estimated particle volume and optical extinction. A refractive index of 1.55 is typical for many organic compounds (Sloane, 1986) but may not represent that of the complex mix of organics in ambient particles. For example, an OC refractive index of 1.46, i0.0 was inferred from measurements at Great Smokey Mountain National Park (Bill Dick, personal communication).

Agreement between measured and estimated Bsp was better under the assumption that OC was completely insoluble (Case 4 versus Case 2 and Case 3 versus Case 1). While the AAE was lower for Case 3 (internal mixture, zero OC water uptake) than for Case 1 (internal mixture, OC water uptake as ethylene glycol), the average estimated Bsp for Case 1 was closer to the average measured Bsp. These differences are probably not large enough to draw meaningful inferences about OC hygroscopic properties at Meadview.

Increasing the OC mass conversion factor from 1.2 (Case 1) to 1.9 (Case 9) increased the AAE from 14.8 to 22.7% and the average estimated Bsp from 10.1 to 12.0 Mm^{-1}. Similarly large effects were obtained by increasing and decreasing the OC density to 1.9 (Case 8) and 0.8 g cm^{-3} (Case 10), respectively. Given a measured size distribution, any assumption which significantly changes the particle volume will similarly affect estimated light scattering. Decreasing the OC refractive index from 1.55 (Case 1) to 1.46 (Case 7) increased the AAE from 14.8 to 15.4% and decreased the average estimated Bsp from 10.1 to 9.7 Mm^{-1}.

The measured filter absorption coefficients (Bap) for Cases 1 and 2 (internal versus external mixture) are compared with the estimated values in Figures 1a and 1b, respectively. Average estimated Bap was higher for the internal mixture (1.49 Mm^{-1}) than for the external mixture (0.87 Mm^{-1}). However, measured Bap was 7 and 12 times higher, on average, than estimated Bap for the internal and external mixture cases, respectively.

The discrepancy between estimated and measured Bap cannot be explained by assumptions about the physical or optical properties of EC. It is also not due to fine-particle dust, which accounted for less than 7% of estimated Bap. If it is assumed that EC exists as a core surrounded by a shell consisting of sulfate, nitrate, OC, and water, average estimated Bap increases by only 5.4%. Increasing the imaginary part of the EC refractive index from 0.6 to 0.9 or decreasing the EC density from 1.7 to 1.0 g cm^{-3} increases the average estimated Bap to 2.1 and 2.4 Mm^{-1}, respectively.

A more likely explanation for the discrepancy between estimated and measured Bap is that there are systematic errors in LIPM Bap measurement. If values smaller than their uncertainties are excluded, the average measured EC absorption efficiency (LIPM Bap/EC concentration) was 38±8 m^2 g^{-1}. There is no theoretical or empirical basis for such a large value (Fuller, 1995). Based on the measured Bsp and Bap, the average single scattering albedo (ω), or Bsp/(Bsp+Bap), was 0.59±0.08. The higher the value of ω, the less absorbing the aerosol. Waggoner et al. (1981) reported values of ω for remote and urban locations based on nephelometer and integrating plate measurements. For remote locations, Anderson Mesa, AZ, Mesa Verde, CO, and Mauna Loa Observatory, average values were 0.91, 0.95, and 0.94, respectively. Values below 0.7 were associated with urban areas. It is difficult to reconcile these and other ω measurements in remote locations (e.g., Bodhaine, 1995) with the measurements at Meadview.

Huffman (1996) and Malm et al. (1996) suggested that high apparent absorption efficiencies (>20 m^2 g^{-1}) measured at remote locations in the IMPROVE network were due to errors in the interpretation of EC and OC concentrations determined by thermal/optical reflectance (Chow et al., 1993). They concluded that this technique identifies material as organic carbon (OC) which is actually light absorbing carbon. However, Huffman (1996) noted that UCD employs an upward correction factor to their LIPM Bap measurements based on of the areal density of mass on the Teflon filter. Recently, Horvath (1997a) calibrated an integrating plate using a white cell to measure extinction and a nephelometer to measure scattering. He found that the integrating plate significantly <u>overestimated</u> Bap when ω was greater than 0.8. This resulted from multiple scattering of incident light out of the path by particles on the filter. A correction algorithm for <u>reducing</u> the measured value to account for this effect was suggested. The fact that the UCD LIPM measurement at Meadview did not reflect this correction, but instead employed an opposite correction, probably explains the high Bap values at Meadview and other IMPROVE sites (Horvath, 1997b).

<u>Extinction Budgets</u>

Extinction budgets were constructed for 12-hour samples at Meadview for which light extinction calculations were made. Estimated scattering for each $PM_{2.5}$ component was obtained for Cases 1 through 5 (Table 2) to represent a range of assumptions about mixing state, sulfate neutralization, and OC water uptake. Light scattering associated with each chemical component was calculated as the product of its compound mass and scattering efficiency. For both internal and external mixtures, the scattering efficiency was calculated by removing 50% of the component's mass and assuming that this changed the particle number but not size. This approach is straightforward for external mixtures and is consistent with our assumption that the particle refractive index can be represented by the volume-weighted average of the refractive indices of the individual components (Lowenthal et al., 1995). The efficiency is the change in scattering divided by the concentration of chemical mass removed.

Coarse-particle scattering was estimated by multiplying the coarse mass concentration (PM_{10} - $PM_{2.5}$) by an efficiency of 0.6 m^2 g^{-1} (Trijonis and Pitchford, 1987; White et al., 1994). Because coarse-particle absorption was not measured and cannot be estimated without information on the coarse size distribution and composition, this component was excluded from the extinction budget. Because we believe that the measured Bap is high-biased, estimated Bap was used to represent fine particle absorption. The final component of the extinction budget is Rayleigh scattering by atmospheric gases, which varies with atmospheric pressure.

The extinction budgets, averaged over the sample set, are presented in Table 3. The variations in the extinction budget are generally small with respect to assumptions about mixing state, sulfate neutralization, and OC water uptake. Although EC scattering and estimated Bap are minor components of extinction, they vary significantly with respect to assumptions about mixing state. On average, Rayleigh, coarse particle, and sulfate scattering were the major components of light extinction, accounting for 39.4, 21.2, and 19.4%, respectively, of reconstructed extinction.

Total path extinction was measured at Meadview with a transmissometer. Malm et al. (1996) presented extinction budgets for Meadview, summer 1992. Although their methodology was different, their results were qualitatively similar to those presented here, except for their treatment of particle absorption. Malm et al. (1996) found that they could only match the measured extinction if the UCD LIPM Bap measurement was used to represent particle absorption. Indeed, the average reconstructed extinction (26.9 Mm^{-1}, Table 3) is significantly lower than the average transmissometer extinction (35.8 Mm^{-1}). If it is the case, as we have argued, that the LIPM Bap is high-biased, then the transmissometer measurement must also be high-biased. Such biases could have resulted from improper calibration of the instrument or atmospheric turbulence along the sight-path. It is probably not possible to resolve problems with the tranmissometer measurements at this time.

<u>Response of Light Extinction to Potential Reduction of MPP Sulfur Emissions</u>

Evaluating the effects of emissions reductions on particle light extinction is straightforward if the effect of such changes on the particle size distribution and composition can be specified. Assuming that MPP contributes to aerosol sulfate, reducing MPP SO_2 will lead to a reduction in aerosol mass and a corresponding reduction in particle light extinction. White (1986) discussed various mechanisms by which gaseous sulfur is oxidized and becomes incorporated into particles. These include: 1) dry oxidation in the gaseous state followed by homogeneous nucleation or diffusion of gaseous H_2SO_4 onto existing particles; 2) diffusion of SO_2 to a dry particle surface followed by oxidation to sulfate on the particle surface; and 3) diffusion of SO_2 into an aqueous haze or cloud droplet followed by oxidation to sulfate in the droplet. When the water in these droplet evaporates, the dry particle sizes increase. Changes in particle size can strongly affect the optical efficiency with which particles scatter and absorb light.

Homogeneous nucleation occurs only at ambient particle concentrations on the order of 10 cm^{-3}, much lower than that expected in the MPP plume or under even remote continental conditions. Therefore, to the extent that MPP SO_2 condenses on or into existing particles, eliminating MPP emissions would be expected to reduce ambient particle sizes. The reality may be much more complicated than any of these scenarios. For example, a reduction in MPP H_2SO_4 could result in an increase in particulate ammonium nitrate as ammonia becomes available to react with gaseous nitric acid.

The reduction in light extinction corresponding to the removal of some or all of a species' mass from the aerosol can be described as a removal efficiency (White, 1986). For sulfate removal, which may be related to a reduction in SO_2 emissions, the removal scattering efficiency is simply:

$$E_{SO4} = \Delta Bsp/\Delta C_{SO4} \tag{2}$$

where ΔC_{SO4} is the concentration of sulfate removed, e.g., as ammonium sulfate. The amount removed is typically taken as a constant fraction as a function of particle size. Zhang et al. (1994) and McMurry et al. (1996) assumed that the effect of removing aerosol mass on particle size followed "growth laws" according to which the particles were originally assumed to have been formed (Seinfeld, 1986; Seinfeld and Pandis, 1998).

Here, we consider growth regimes which characterize growth limitation by three mechanisms: 1) the transition regime, where growth of particles 0.01-0.2 μm in diameter is limited by gaseous diffusion to the particles; 2) surface reaction, where growth is limited by reactions on the particle surface; and 3) volume reaction, where growth is limited by reactions in the particle volume, e.g., in a haze or cloud droplet. The fraction of mass removed as a function of particle diameter (D) is proportional to $D\beta$, D^2, or D^3, multiplied by the number of particles in each size bin (i.e., with diameter D), for the transition, surface reaction, and volume reaction regimes, respectively. For the transition regime, β is related to the particle diameter and the air mean free path (λ=0.0651 μm, Seinfeld and Pandis, 1998):

$$\beta = (1+Kn)/(1+1.71Kn+1.33Kn^2) \tag{3}$$

where Kn, the Knudsen number, is equal to $2\lambda/D$.

The MPP contribution to aerosol sulfate was estimated on a case-study basis with integrated dispersion (Yamada, 1996) and chemistry (Seigneur et al., 1997) models. The maximum 12-hour contribution of MPP to sulfate at Meadview was 19% on 14 August, 1992, for the 12-hour period beginning at 1900 MST (Pitchford et al., 1999). In this case, sulfate was assumed to have been formed by dry oxidation of SO_2 in the MPP plume. Particle growth would have been limited by diffusion of gaseous H_2SO_4, i.e., in the transition regime.

The IMPROVE concentrations of $PM_{2.5}$ sulfate, nitrate, OC, EC, dust, and coarse-particle mass for the Meadview sample on 14 August (1900 MST) were 1.77, 0.041, 1.05, 0.059, 0.34, and 5.6 $\mu g/m^3$, respectively and the 12-hour average relative humidity was 26%. Light scattering and absorption were estimated assuming a homogeneous internal mixture of sulfate, nitrate, OC, and EC and an external mixture of fine dust. The MOUDI data for the day time sample on 14 August were used to represent the night time size distributions. Total extinction was estimated by adding coarse-particle and Rayleigh scattering to the estimated fine-particle scattering and absorption. Because the growth functions are continuous, ammonium sulfate was removed in small increments (0.19*1.375*1.77/ 100) and the particle size distribution was recalculated at each step.

The initial results did not strictly conform to either the transition or surface reaction regime. That is, given the measured size distribution, preferentially removing mass from the three smallest size bins (out of sixteen bins) under these regimes caused the remaining mass to be negative. In other words, the measured size distribution did not conform to the growth laws. While it is possible that particle growth for this sample was actually limited by a volume-controlled reaction, we evaluated the effects of mass removal under modified growth regimes. If the remaining sulfate concentration in a size bin became negative, we constrained it to zero, added the negative residual to the next removal increment, and continued to remove sulfate mass from the larger size bins as a function of D according to the growth law. This algorithm allows for removal of any specified sulfate mass concentration and for comparing removal efficiencies for different particle growth mechanisms as a function of particle diameter.

The results are presented in Table 4. The ammonium sulfate removal efficiency is smallest for transition regime growth because material is preferentially removed from the smaller particles. Conversely, efficiencies are highest for the volume reaction regime and for removing sulfate mass in equal fractions from each size bin. The latter two cases would be equivalent if the fractional ammonium sulfate volume was constant across size bins. While the maximum difference in removal efficiencies is significant (3.06-1.89 / 1.89 = 62%), the percent reductions in Bsp and Bep are less dramatic, ranging from 7.2-11.7 and 3.3-5.3%, respectively.

CONCLUSIONS

MOUDI size-resolved and IMPROVE aerosol chemical data collected at Meadview, AZ during Project MOHAVE were used to estimate particle light extinction. Variations in particle size appeared to be related relative humidity. Light scattering was estimated using Mie theory to within about 15%. Large discrepancies (factors of 7-12) between estimated and measured Bap are attributed to systematic errors in the laser integrating plate Bap measurements. Light extinction estimates were largely insensitive to assumptions about aerosol mixing state, degree of sulfate neutralization, and organic carbon hygroscopic properties. The major components of reconstructed light extinction were Rayleigh scattering (39.4%), scattering by coarse particles (21.2%), and scattering by fine sulfate (19.4%) and organic carbon (8.6%) particles. It was also estimated that an MPP sulfur dioxide emissions reduction leading to a 19% decrease in ambient sulfate concentration would result in a 3.3 to 5.3% reduction in total light extinction, depending on assumptions about how such removal would affect the particle size distribution.

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Table 1. Physical and optical properties of aerosol chemical components

Species	Mass Factor[a]	Density	Refractive Index
H_2SO_4	1.021	1.84	1.44, i0.0
$(NH_4)_2SO_4$	1.375	1.76	1.53, i0.0
NH_4HSO_4	1.198	1.78	1.47, i0.0
NH_4NO_3	1.29	1.73	1.55, i0.0
OC	1.2[b]	1.2[b]	1.55, i0.0[b]
EC	1.0	1.7	1.90, i0.6
Soil	1.0	2.3	1.53, i0.005

[a] Factor to convert ion and carbon mass to compound mass.
[b] These values were varied in sensitivity tests.

Table 2. Sensitivity of estimated Bsp to assumptions about mixing state, sulfate neutralization, and OC water uptake, mass conversion factor, density, and refractive index.

Case	Mix[a]	Sul[b]	OC H_2O[c]	OC Factor[d]	OC Density.	OC RI[e]	AAE (%)[f]	Bsp[g]
1	Int	M	EG	1.2	1.2	1.55	14.8	10.1
2	Ext	M	EG	1.2	1.2	1.55	14.7	10.4
3	Int	M	0	1.2	1.2	1.55	14.4	9.9
4	Ext	M	0	1.2	1.2	1.55	13.8	10.1
5	Int	H	EG	1.2	1.2	1.55	15.0	9.9
6	Int	H	0	1.2	1.2	1.55	14.6	9.7
7	Int	M	EG	1.2	1.2	1.46	15.4	9.7
8	Int	M	EG	1.2	1.9	1.55	18.2	8.9
:9	Int	M	EG	1.9	1.2	1.55	22.7	12.0
10	Int	M	EG	1.2	0.8	1.55	21.8	12.0

[a] Mixing state: internal (Int) or external (Ext).
[b] Sulfate neutralization: based on MOUDI (M) or HEADS (H) sampler.
[c] OC water uptake: as ethylene glycol (EG) or no water uptake (0).
[d] OC mass conversion factor.
[e] OC refractive index.
[f] Average absolute error.
[g] Measured fine Bsp.

Table 3. Meadview, summer 1992 extinction budgets (Mm^{-1}).

	Scattering							
Case[a]	Sulfates	Ammonium Nitrate	OC	EC	Fine Dust	Coarse Particles	Rayleigh	Fine Particle Absorption
1	5.4	0.64	2.3	0.26	0.87	5.7	10.6	1.49
2	5.1	0.62	2.6	0.43	0.87	5.7	10.6	0.87
3	5.4	0.64	2.1	0.26	0.87	5.7	10.6	1.49
4	5.1	0.62	2.4	0.43	0.87	5.7	10.6	0.87
5	5.1	0.65	2.3	0.29	0.87	5.7	10.6	1.49
Ave.	5.2	0.63	2.3	0.33	0.87	5.7	10.6	1.24
%	19.4	2.3	8.6	1.23	3.2	21.2	39.4	4.6

[a] From Table 3.

Table 4. Effects of removing MPP sulfate for Meadview sample collected on 14 August 1992 (1900-0700 MST).

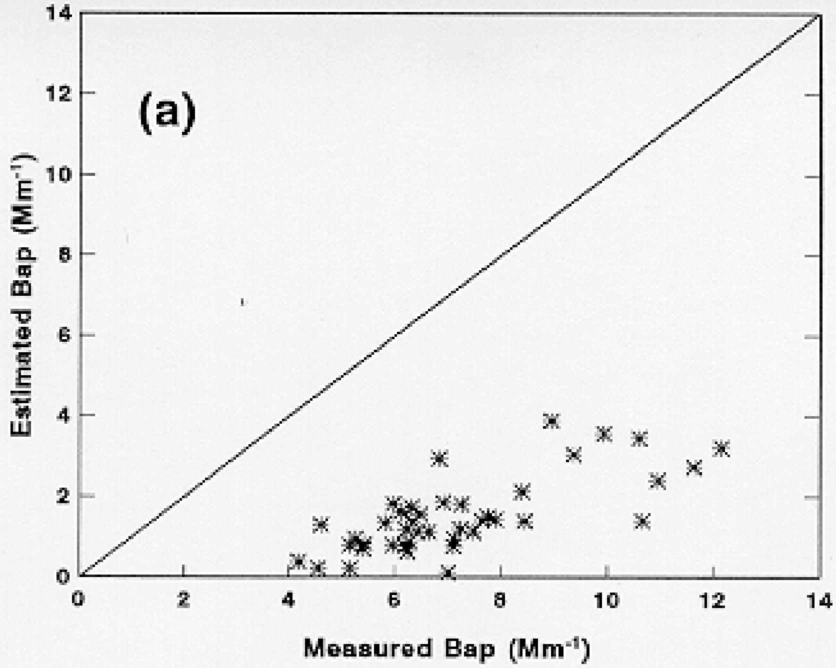
Estimated Extinction	
$PM_{2.5}$ Bsp[a]	12.01
$PM_{2.5}$ Bap[b]	0.64
Coarse Bsp[c]	3.36
Rayleigh	10.6
Total	26.61

Growth Regime	Efficiency (m^2/g)[d]	% Reduction in Scattering	% Reduction in Extinction
Transition	1.89	7.2	3.3
Surface Reaction	2.29	8.8	4.0
Volume Reaction	2.91	11.2	5.1
Equal Fractions[e]	3.06	11.7	5.3

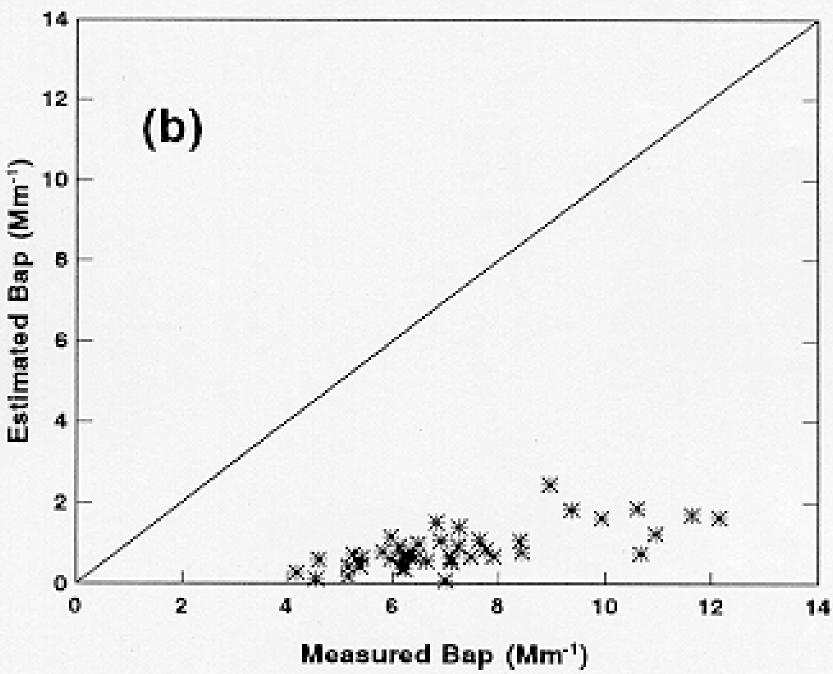
[a] Estimated $PM_{2.5}$ Bsp.
[b] Estimated $PM_{2.5}$ Bap.
[c] Estimated coarse scattering (as described above).
[d] Ammonium sulfate removal scattering efficiency.
[e] 19% of the sulfate concentration in each size bin was removed.

FIGURE CAPTIONS

1. Measured $PM_{2.5}$ Bap versus Estimated Bap: a) homogeneous internal mixture; b) external mixture.



(a)
Estimated Bap (Mm-1)
Measured Bap (Mm-1)
0
2
4
6
8
10
12
14



(b)
Estimated Bap (Mm-1)
Measured Bap (Mm-1)
0
2
4
6
8
10
12
14